Identification and Determination of Some Trace Organic Compounds in Coastal Seawater of Northern Greece

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During recent years, an increased concentration of many organic compounds has been noticed in coastal waters close to industrialized and urbanized areas. The sources of these compounds mainly originate from domestic industrial and agricultural effluents.

It is apparent that the conventional measurements of organic chemical pollution (BOD, COD, TOC) do not always reveal the true amount of environmental pollution. The need for identification and determination of specific organic contaminants by using modern instrumental techniques is obvious.

In the present paper, a combination of gas chromatography - mass spectroscopy (GC/MS) was used to identify and determine traces of organic compounds in coastal seawater samples taken from two gulfs with increased marine pollution. These gulfs were Thermaikos and Kavala, which are located in Northern Greece. The former is situated close to a large city, Thessaloniki, and a large industrial area, including a refinery unit. The latter is close to a smaller city, Kavala, which is rapidly developing due to off-shore oil wells.

Previous investigations in those areas have shown high heavy metal concentrations in seawater, sediment and marine organism samples (Vasilikiotis et al. 1983 ;Fytianos et al. 1983).

In the Thessaloniki Gulf (Fig. 1), we installed six sampling stations. Stations 1 and 2 were located in the industrial area and in the harbor, respectively. Station 3 was esteablished in the area where untreated municipal sewage from the city of Thessaloniki is mainly discharged (about 80,000 m^3/24 h), and stations 4, 5 and 6 were established in areas where no wastewater discharge occurs. In the Gulf of Kavala (Fig. 2), we installed four sampling stations:station 1 in the harbor, station 2 near the industrial area, station 3 in the middle of the gulf and station 4 2kms away from the off-shore oil well platform.
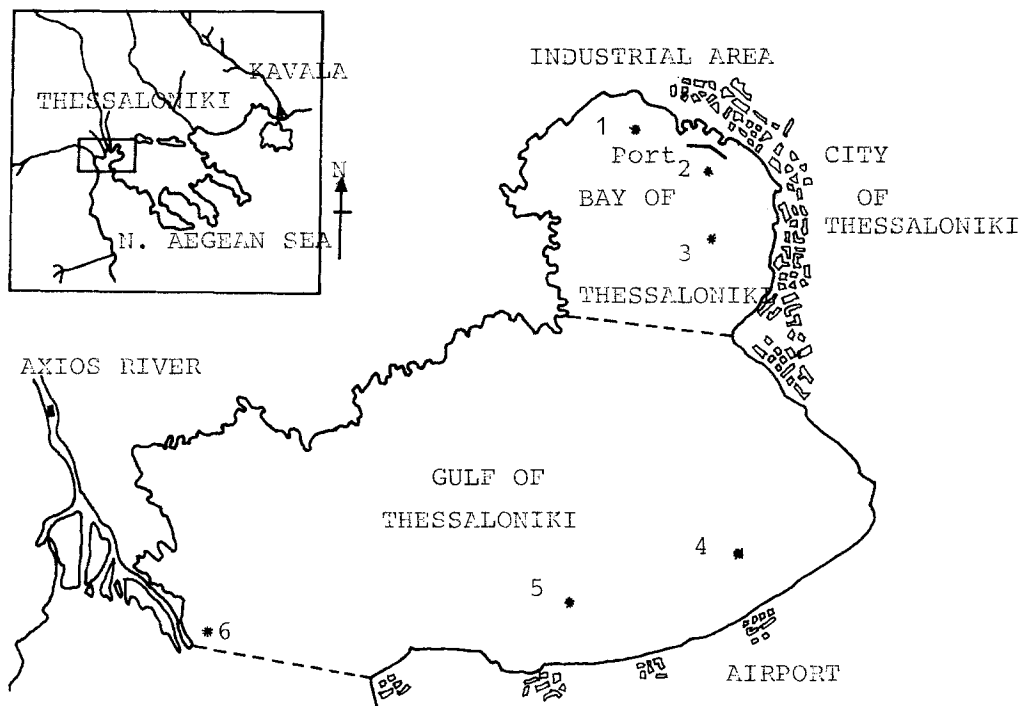
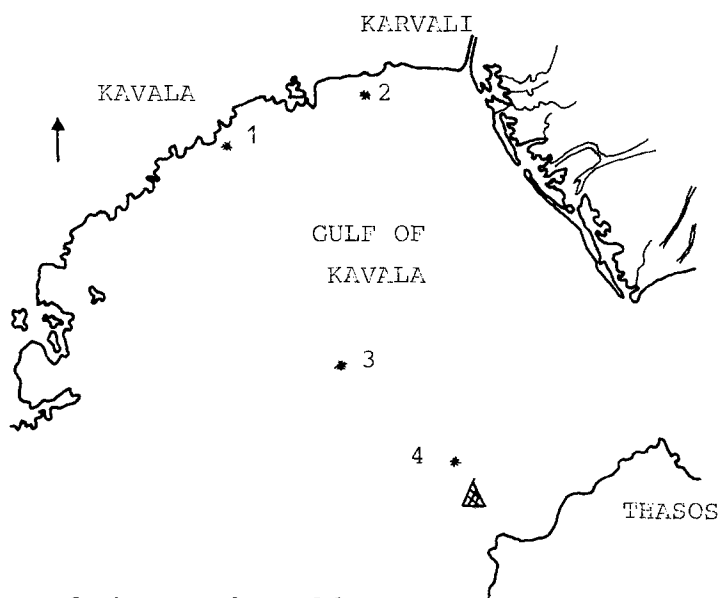Fig. 1. Map of the Thermaikos gulf

Fig. 2. Map of the Kavala gulf

MATERIALS AND METHODS

During a period of two years, 1981 and 1982, water samples were
collected twice a month from the Thermaikos and Kavala Gulf sta-
tions. The identified organic compounds were organochlorine pe-
sticides, polycyclic aromatic hydrocarbons(PAH),slightly volatile
halogenhydrocarbons and polychlorinated biphenyls. Organochlori-
ne pesticides and polychlorinated biphenyls were determined by
GC/MS, the slightly volatile halogenhydrocarbons by GC and poly-
cyclic aromatic hydrocarbons were analysed by the two-dimensional
TLC (Klein et al. 1979).

A Hewlett - Packard GC/MS system, model 5709A, was used to identi-
fy and determine organic compounds. In addition, this unit was
equipped with a data system. All reagents used were supplied by
Merck A.G.

Surface seawater was sampled into 2.5-L glass containers. Through
the process of filtration, the suspended solids were removed, and
an exact volume of filtrate (2 L) was mixed with 20 mL of n-hexane.
This mixture was strirred for a period of 12 hr in a glass contai-
ner into which a microseparator was inserted (Fig. 3) to enable
direct extraction of pesticides. This instrument consists of two
tubes. Through the first tube, the one possessing the funnelshaped
top, distilled water, free of pesticides, was added until the n -
hexane layer rose to the desired height in the second tube (Weil
et al. 1974). From this tube, an aliquot of 15 mL of the separa-
ted n - hexane layer was transferred to a rotary evaporator. This
volume was reduced without heating to about 1 mL;the container
was rinsed with 1 mL of n - hexane and the total volume of 2 mL
was cleaned by silica gel column chromatography. After this final
step, the identification of organochlorine pesticides was perfor-
med by GC/MS technique (Garrison et al. 1978;Shinohara et al.1981)
and their determination by GC with a linear electron-capture dete-
ctor (ECD). The samples were analysed for aldrin, chlordane, DDT,
dieldrin, heptachlor, methoxychlor, lindane and the PCB group.

For the polycyclic aromatic hydrocarbons determination, an exact
volume of the above filtrated sample (2 L) was mixed with 40 mL
of cyclohexane and strirred for 2 hr. After direct extraction by
the microseparator, the extract was concentrated to approximately
0.5 mL. If the extract was of a yellow or brown color, then puri-
fication was necessary on a chromatographic column of aluminium
oxide. Determination was performed by using the technique of two-
dimensional TLC. The separated spots became visible by using a
UV lamp. In view of the characteristic coloring and the position
due to their Rf values,the spots could be identified by compa-
ring them to a similar chromatogram from an artificial standard
solution of the analysed substances. The samples were analysed
for fluoranthene ($C_{16}H_{10}$), 3,4 - Benzpyrene ($C_{20}H_{12}$), 3,4 - Benz-
fluoranthene ($C_{20}H_{12}$), 1,12 - Benzperylene ($C_{22}H_{12}$), 11,12 - Benz-
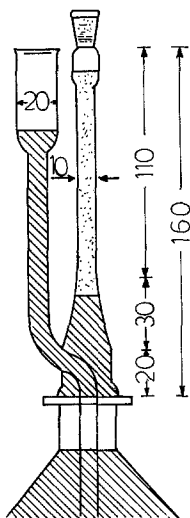fluoranthene ($C_{20}H_{12}$) and Indeno(1,2,3-cd)pyrene ($C_{22}H_{12}$).

Fig.3. A microseparator
for the direct extraction
of organochlorine pestici-
des (Dimensions in mm).

For the slightly volatile halogenhydro-
carbon determination, a volume of 250
mL of filtrated sample was mixed with
5 mL of cold pentane and stirred for
5 min at 0 C. After a dividing the ex-
traction with the microseparator, the
extract was analysed by gas chromato-
graphy.

RESULTS AND DISCUSSION

The concentrations of organochlorine
compounds in water which are presented
in Table 1 illustrate the general le-
vels found in the waters of Thermai-
kos and Kavala Gulfs. From the analy-
sed samples lindane p, p'- DDT, diel-
drin and PCBs were found in trace a-
mounts. In the same samples and espe-
cially in the harbor areas of Thessa-
loniki and Kavala, the concentration
of the organochlorine compounds was
higher. The polycyclic aromatic hy-
drocarbons were found in both unpol-
luted and polluted areas of the Thes-
saloniki and Kavala Gulfs;in the first
case their concentrations ranged from 10 to 25 ng/L. The concentra-
tion was estimated for the total of the six polycyclic aromatic hy-
drocarbons. In polluted areas (industrial regions, harbors and off-
shore oil platform in the Kavala Gulf), the samples contained poly-
cyclic aromatic hydrocarbons in concentrations of 80 ng/L. These
values compared to those reported in the literature on this subject
are relatively close to those found for unpolluted and slightly pol-
luted areas, respectively. Of these six polycyclic aromatic compounds,
fluoranthene was identified in higher concentrations.

From the analysed samples, only tetrachlorethene and trichlorethene
were identified in higher concentrations in the harbor areas of Thes-
saloniki (station 2) and Kavala (station 1) and near the off - shore
oil platform (station 4). The concentrations varied from 0.25 to 3
µg/L. If we compare these values with the permissible values for
drinking water in West Germany (limit value 50 µg/L) and the EEC
standards (1 µg/L), we can conclude that this pollution is low
according to the former's standards but not to those of the latter.

Hence from the data obtained in this preliminary study, we can ge-
nerally conclude that some organic compounds which were identified
existed at a concentration range of ng/L which is still comparati-
vely low. However particularly high concentrations were observed
in highly industrialized regions and near the off-shore oil plat-
form, where there is always the possibility of marine pollution,

Table 1. Organochlorine compounds in water samples of Thermaikos and Kavala Gulfs. (ng/L) (mean values).

Sampling area	Lindane	p,p'-DDT	Dieldrin	PCB	PAH	$Cl_2C=CCl_2$ (µg/L)	$Cl_2C=CHCl$ (µg/L)
Thermaikos Gulf							
St_1	0.12	1.5	0.9	3.1	65	1.80	1.65
St_2	0.08	1.2	1.1	2.8	49	2.10	2.30
St_3	0.01	1.3	0.8	2.6	40	0.52	0.61
St_4	0.01	0.8	0.2	1.4	17	0.31	0.28
St_5	0.03	0.6	0.2	1.8	10	0.27	0.26
St_6	0.02	0.4	0.3	2.1	25	0.41	0.35
Kavala Gulf							
St_1	0.07	0.9	0.6	2.1	55	2.50	2.10
St_2	0.05	1.2	0.4	1.8	34	1.80	1.70
St_3	0.02	0.4	0.2	1.2	27	0.39	0.35
St_4	0.11	0.8	0.8	2.7	80	3.00	2.80

due to oil discharge. While the values which were found, indeed show the presence of environmental organic pollutants, the concentration of the compounds has not yet reached threatening levels.

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